333. *The Oxidation of Monoethenoid Fatty Acids and Esters. The Union of Gaseous Oxygen with Erucic Acid and Methyl and* n-*Propyl Erucate.*

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The methods of preparation of highly purified erucic acid and its esters have been studied. Catalytic oxidation of the pure acid and of methyl and *n*-propyl erucate at various temperatures has been investigated, and the nature of the complex changes occurring studied. The oxidations at high temperatures result in rapid hydroperoxide decomposition followed by some dimerisation, and there is evidence that at moderate temperatures the mechanism may follow a different course, as in the case of other monoethenoid fatty acids. The composition of the oxidation products varies considerably with conditions of oxidation and, in oxidations of the esters, the presence of the terminal alkyl group apparently has considerable influence, not only on the rate of entry of the oxygen, but also on that of decomposition of the hydroperoxides.

THE disruptive oxidation of erucic acid was first carried out by Dorée and Pepper (*J.*, 1942, 477) who found that oxidation of the *cis*- and the *trans*-form with various oxidising agents cleaved the carbon chain or gave oxido-complexes to a degree varying with the conditions. In the action of gaseous oxygen on erucic acid with and without catalysts at 70° and 120° they concluded that oxido-compounds formed 12—15% of the oxidation products; they suggested that unstable peroxides might be amongst the initial oxidation products, and that from them aldehydic compounds might be formed which polymerised to resistant, brown, oily residues. The formation and decomposition of hydroperoxides of erucic acid and its methyl esters during autoxidations were not investigated by Dorée and Pepper, and the mechanism of autoxidation of this monoethenoid fatty acid has not yet been fully elucidated.

The object of the work now described was to study the catalytic oxidation of pure erucic acid and its methyl and *n*-propyl esters at various temperatures, *viz.*, 55°, 85°, and 120°, and to investigate the nature of the changes taking place at all stages of oxidation—in particular to study hydroperoxide formation and transition at moderate and at high temperature. The oxidations with gaseous oxygen were therefore carried out with catalysts—in the form of soaps of the transition metals—by which means efficient oxidation without dimerisation and polymerisation is obtained comparatively quickly.

For this investigation samples of the acid and its esters were required to be free from polyethenoid fatty acids, the presence of which would modify the course of autoxidation (Hilditch, *Nature*, 1950, **166**, 599).

Separation of erucic acid from the mixed fatty acids of rape seed oil was formerly investigated by Dorée and Pepper (*loc. cit.*). Crystallisation of the mixed acids from alcohol was followed by fractional precipitation of the lead salts from alcoholic solution, insufficient lead acetate for complete precipitation being used (Taufel and Bauschinger, *Z. angew. Chem.*, 1928, **41**, 157).

The separation of erucic acid from rape oil fatty acids involves the removal of (1) saturated fatty acids such as behenic, (2) other monoethenoid fatty acids such as oleic, and (3) more highly unsaturated acids such as linoleic. Saturated fatty acids can be removed by fractional precipitation of the lead salts, but we were not able to secure their complete elimination by a single precipitation (cf. Dorée and Pepper, *loc. cit.*). Oleic and linoleic acids can be eliminated from rape oil acids by repeated crystallisation from alcohol, but the comparatively low melting point of erucic acid (33·8°) limits the useful temperature range. Lead erucate separates as a liquid from hot alcoholic solutions, particularly if lead oleate is also present. Lithium erucate, however, is freely soluble in boiling alcohol, but almost completely precipitated at room temperature. The lithium salts of the saturated acids are also sparingly soluble in alcohol at room temperature, but those of oleic acid and of the more highly unsaturated acids are more soluble.

The method finally adopted was to precipitate the insoluble lithium salts, recrystallise them several times from alcohol, and finally to remove saturated acids by fractional precipitation of the lead salts. The product was pure erucic acid, completely free from polyethenoid acids.

The results of catalytic oxidations of pure erucic acid with uranium erucate as catalyst now show that the general trend of oxidation is similar to that for elaidic acid and its methyl and *n*-propyl esters but with certain modifications. The changes in the observed active-oxygen content during the oxidation of each of these acids and their esters were similar, *i.e.*, a rise to a maximum followed by decomposition, but the percentage of active oxygen corresponding to these maxima was found to be highest in autoxidised propyl erucate, whereas in former work on elaidic acid and its esters (Skellon and Thruston, *J.*, 1949, 1626) highest values were obtained during oxidation of the methyl esters. In the early stages the autoxidations at 120° and 85° were exothermic as the peroxide value was increasing, the thermostatically controlled oven having to be kept a few degrees below the desired temperature with carefully controlled mechanical stirring; this thermal effect was particularly noticeable in the case of erucic acid oxidised at 120° where the peroxides were rapidly decomposed. It is of interest to compare the molar fraction of hydroperoxide present, as measured by the peroxide value, with the fraction oxidised, as measured by the fall in the iodine value (both values being taken at the stage of maximum peroxide-oxygen, content) :

At 120°.	Propyl ester	Methyl ester	Acid
(1) Peroxide (molar fraction)	0·325	0·084	0·024
(2) Oxidation (molar fraction)	0·42	0·34	0·24
Ratio (1)/(2)	0·775	0·246	0·100

These results clearly indicate the greater stability of the peroxides of the esters.

The general trend of oxidation of erucic acid and its esters at 85° and 120° appeared to be similar. The changes in peroxide-oxygen content during oxidation of methyl and *n*-propyl erucate at 85° were comparable with those observed during oxidation of methyl and *n*-propyl elaidate at the same temperature (Skellon and Thruston, *loc. cit.*), and the stability of the ester hydroperoxides was again evident. At 55° the rate of oxidation was much slower and the reaction at this temperature probably follows a different course; *e.g.*, oxidation of the acid resulted in an appreciable fall in iodine value with little peroxide formation, whilst in oxidation of the propyl ester the peroxide value changed rapidly with little fall in iodine value.

Molecular-weight determinations indicated some dimerisation at all temperatures. This was confirmed by the fall of the acid value during oxidations of the free acid, indicating that the carboxyl group had taken part in the condensation. The esters increased in viscosity, but the acid, after oxidation at 85° and 120°, gave a product which was liquid at room temperatures. Little carbon dioxide was evolved during the short autoxidations.

The saponification values of the oxidised esters appeared to increase normally with the time of oxidation. There was evidence, however, that a proportion of the oxidation product breaks down to a considerable extent on saponification—probably owing to rupture at the ethenoid linkage.

Influence of the presence of alkyl groups in the molecule was very marked, the peroxide values in ester oxidations always being considerably higher. The results appear to support present views that initial attack at temperatures above 100° takes place directly at the ethenoid linkage, with subsequent migration of the ethenoid linkage and formation and decomposition of isomeric hydroperoxides, resulting in formation of complex oily products containing ketonic groups. It is noteworthy that the ketonic derivatives invariably formed in these and other high-temperature catalytic oxidations of monoethenoid fatty acids and esters are apparently secondary oxidation products of a different character from the unsaturated keto-acids found by Ellis (*Biochem. J.*, 1950, **46**, 129) in autoxidation of oleic and elaidic acid at lower temperatures. The exact nature of the numerous complex products resulting from catalytic oxidation of the various monoethenoid fatty acids and esters is now being systematically investigated, and the results should throw considerable light on later stages of the oxidation mechanism.

EXPERIMENTAL

Preparation of Eurcic Acid.—*First preparation.* High-grade rape seed oil (800 g.; sap. val., 172·0; I.V., 100·7) was dissolved in alcohol (1 l.) and mixed with a solution of potassium hydroxide (200 g. in 100 ml. of water). After the solution had been heated for 5 hours on a water-bath, the alcohol was distilled off, boiling water added (1 l.), and the liquid acidified; the free fatty acids separated. The aqueous layer was then removed as completely as possible and the fatty acids were washed several times with boiling distilled water. The recovered fatty acids (725 g.; acid val., 187·9; I.V., 108·9) were dissolved in alcohol, heated to boiling, and mixed with a boiling solution of lead acetate (50 g.) in alcohol (200 ml.) containing 1·5% of acetic acid. Next morning, the solid lead salts were filtered off. The mother-liquors were similarly treated and each successive crop of lead salts was converted into free fatty acids, which were washed repeatedly with hot water.

Each batch of free fatty acids was then separated into less soluble and more soluble lead salts by fractional crystallisation. A suitable amount of lead acetate being used, this process was repeated until the following fractions of free fatty acids were obtained:

Fraction	Wt., g.	M. p.	Acid val.	I.V.	Fraction	Wt., g.	M. p.	Acid val.	I.V.
1	25	50°	166	46	5	200	Pasty liquid	—	89·5
2	5	44	166	—					
3	4	47	166	—	6	79	Clear liquid	—	90
4	105	33	165·9	71					
					7	70	,,	—	98

After further crystallisation of the lead salts of Fraction No. 4 there were recovered 90 g. of pure erucic acid, m. p. 33·0°, n_{D}^{50} 1·4512 (Found: acid val, 165·9; I.V., 74·5. Calc. for $C_{22}H_{42}O_2$: acid val., 165·8; I.V., 75·0).

Second preparation (*modified process*). Fatty acids (730 g.; acid val., 188·9; I.V., 106·9) from rape oil were dissolved in alcohol (2 l.), heated to boiling, and neutralised with a solution of lithium hydroxide. After being kept overnight at room temperature, the insoluble lithium salts were filtered off, recrystallised from aqueous alcohol (1 : 1), and converted into fatty acids by agitation with dilute hydrochloric acid. Recovered crude erucic acid (319 g.) (Found: acid val., 164; I.V., 65·0. Calc. for $C_{22}H_{42}O_2$: acid val., 165·8; I.V., 75·0) was dissolved in hot alcohol (1 l.) and to this was added a solution of lead acetate in alcohol (20 g. in 1 l.) containing a little acetic acid. Next morning, the precipitated lead salts were separated, and the fatty acids (295 g.) recovered from the mother-liquor (Found: acid val., 165·4; I.V., 74·6).

Preparation of Methyl Erucate.—Pure erucic acid (20 g.), methyl alcohol (100 ml.), and concentrated sulphuric acid (2 ml.) were refluxed for 2 hours, excess of alcohol was distilled off, and the residue was poured into water and extracted with light petroleum. After treatment with sodium carbonate solution, the petroleum solution was washed and dried, and the solvent removed; the ester (20 g.) had $n_{\mathrm{D}}^{15\cdot5}$ 1·4575, n_{D}^{50} 1·449 (Found: acid val., 0·2; sap. val., 159; I.V., 68·6. Calc. for $C_{23}H_{44}O_2$: sap. val., 159·2; I.V., 72·1).

Preparation of Propyl Erucate.—Pure erucic acid (30 g.), *n*-propyl alcohol (100 ml.), and concentrated sulphuric acid (2 ml.) were refluxed for 2 hours. After neutralisation with alcoholic potash, the solution was diluted with water (200 ml.) and extracted with light petroleum. After the extract had been washed and dried, removal of the solvent gave propyl erucate (25 g.), $n_{\mathrm{D}}^{15\cdot5}$ 1·4556, n_{D}^{50} 1·4429 (Found: acid val., 0·1; sap. val., 147·5; I.V., 63·0. Calc. for $C_{25}H_{48}O_2$: sap. val., 147·5; I.V., 66·7).

Catalytic Oxidations.—Oxidations were carried out in Pyrex boiling tubes, with a glass stirrer of paddle type, a bubbler tube with drawn-off jet for entry of oxygen, and a thermometer. The tubes were inserted through the top of an electric oven (thermostatic control). The oxidations, which were exothermic in the early stages, were sensitive to the rate of stirring, which was therefore kept uniform. The rate of flow of oxygen was also kept constant throughout the series of oxidation (60 bubbles per minute).

(i) *Of erucic acid.* Oxidations of pure erucic acid prepared as detailed were carried out with use of 0·05% of U (as uranium erucate) as catalyst. The results of oxidations at 120°, 85°, and 55° are given in Table 1. All peroxide values are expressed as active oxygen (%). There was slight reduction of Fehling's solution at the end of the heating at 120° and 85°, but none after that at 55°; the molecular weights (by Rast's method) of the final products were 378, 354, and 400, respectively (Calc. for $C_{22}H_{42}O_2$: *M*, 338).

TABLE 1. *Catalytic oxidation of erucic acid.*

At 120°.	Time (hours)	1	2	3	4	5	6	7
	I.V.	69·3	61·3	57·3	—	46·9	39·7	36·5
	Acid val.	165	157	152	151	145	—	143
	Active oxygen, %	0·03	0·08	0·11	$0{\cdot}09_4$	0·06	0·026	0·017
	n_{D}^{50}	1·4525	1·4530	1·4540	1·4562	1·4569	1·4577	1·4582
At 85°.	Time (hours)	1	2	4	8	12	16	21
	I.V.	67·2	64·4	63·0	55·7	50·1	45·8	42·3
	Acid val.	159	157·5	158	153	150	149	144
	Active oxygen, %	—	0·17	0·175	0·30	0·29	0·36	0·17
	n_{D}^{50}	1·4507	1·4512	1·4517	1·4531	1·4539	1·4536	1·4545
At 55°.	Time (hours)	4	8	12	16	20	23·5	
	I.V.	65·1	64·2	62·4	51·2	42·1	—	
	Acid val.	160	160	159	157	162	161	
	Active oxygen, %	0·05	0·06	0·09	0·105	0·112	—	
	n_{D}^{50}	1·4514	1·4522	1·4514	1·4516	1·4516	—	

(ii) *Of methyl erucate.* This was carried out under the same conditions as for the acid, and the results are given in Table 2. Reduction of Fehling's solution was rapid after the final heating at 120°, slight after that at 85°, and nil after that at 55°, and the molecular weights (Rast's method) were 352, 362, and 346, respectively (Calc. for $C_{23}H_{44}O_2$: *M*, 352).

TABLE 2. *Catalytic oxidation of methyl erucate.*

At 120°.	Time (hours)	1	2	3	4	5	7	7·75
	I.V.	63·8	61·3	56·6	53·4	47·7	39·1	29·3
	Sap. val.	165	175	177	—	196	202	212
	Active oxygen, %	0·10	0·18	—	0·32	0·35	0·24	0·17
	n_{D}^{50}	—	1·4588	1·4594	1·4599	1·4598	1·4610	1·4613
At 85°.	Time (hours)	1	2	4	8	12	16	21
	I.V.	64·2	64·7	64·3	60·9	59·4	57·6	51·3
	Sap. val.	161	161	162	163	162·5	164	173
	Active oxygen, %	—	0·10	0·10	0·16	0·19	0·38	0·60
	$n_{\mathrm{D}}^{15\cdot5}$	1·4579	1·4580	1·4581	1·4581	1·4583	1·4587	1·4588
At 55°.	Time (hours)	4	8	12	16	20	23·5	
	I.V.	63·8	64·8	63·7	63·7	62·3	63·4	
	Sap. val.	166	172	161	164	172	165	
	Active oxygen, %	0·035	0·038	0·043	0·060	0·052	—	
	$n_{\mathrm{D}}^{15\cdot5}$	1·4577	1·4568	1·4573	1·4569	1·4575	1·4572	

(iii) *Of propyl erucate.* The results obtained under the same conditions are given in Table 3. The reduction of Fehling's solution by the final products of the runs at 120°, 85°, and 55° was rapid, slight, and negative, respectively, and the corresponding values of *M* (by Rast's method) were 362, 368, and 420 (Calc. for $C_{25}H_{48}O_2$: *M*, 380).

TABLE 3. *Catalytic oxidation of propyl erucate.*

At 120°.	Time(hours)	2	4	6	8	10	12	17	21	23
	I.V.	57·6	55·5	50·6	49·1	44·0	38·4	—	33·2	—
	Sap. val.	140	142	156	166	183	192·5	244	275	—
	Active oxygen, %	0·44	0·65	0·90	1·26	1·2	1·05	1·08	0·76	0·49
	$n_{\mathrm{D}}^{15\cdot5}$	1·4565	1·4574	1·4579	1·4581	1·4584	1·4590	1·4603	1·4611	—
At 85°.	Time (hours)	1	3	6	9	12	15	18	20	23
	I.V.	62·0	62·0	58·7	59·8	57·2	56·4	51·4	—	45·0
	Sap. val.	149	156	161	167	169	163	145	—	161
	Active oxygen, %	0·03	0·07	0·16	0·25	0·34	0·50	0·51	0·66	0·69
	$n_{\mathrm{D}}^{15\cdot5}$	1·4567	1·4562	1·4569	1·4573	1·4577	1·4579	1·4580	—	1·4580
At 55°.	Time (hours)	1	2	4	8	12	16	20	24	
	I.V.	—	—	60·9	60·5	61·5	—	62·7	62·2	
	Sap. val.	—	—	146	147	150	150	156	—	
	Active oxygen, %	0·05	0·07	0·17	0·26	0·20	0·35	0·20	0·11	
	$n_{\mathrm{D}}^{15\cdot5}$	—	—	1·4569	1·4570	1·4569	1·4516	—	1·4567	

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